Dissolution of Magnesium from Serpentine Mineral in Sulfuric Acid Solution

Kyoungkeun Yoo, Byung-Su Kim, Min-Seuk Kim, Jae-chun Lee* and Jinki Jeong

Minerals & Materials Processing Division, Korea Institute of Geoscience & Mineral Resources (KIGAM), Daejeon 305-350, Korea

As the volume of CO2, one of greenhouse gases linked to global warming, in the atmosphere increases, there has been an increasing interest in CO2 sequestration. Aqueous carbonation, which involves the extraction of Mg from serpentine minerals and the subsequent carbonation reaction with CO2 to form the geologically stable mineral MgCO3, has been proposed as a promising CO2 sequestration technology. This study investigates the dissolution of Mg from serpentine mineral in H2SO4 solution. The study is part of a major research project aimed at developing an effective CO2 sequestration technology using the serpentine mineral which is readily available in Korea. Complete dissolution of Mg from natural serpentine was achieved in 30 min at a temperature of 90°C under 0.5 M H2SO4. The rate of dissolution of Mg was independent of the agitation speed at speeds above 300 rpm. The fraction of Mg dissolved from milled serpentine was found to be a little higher than that from natural serpentine up to 70°C in 0.5 M H2SO4. The Fanger equation was used to explain the dissolution rate data. The rate of Mg dissolution seemed to be limited by diffusion through the thin channels formed between the silica layers in the serpentine particles.

1. Introduction

Serpentine mineral [Mg3Si2O5(OH)4] is a hydrous magnesium-rich silicate mineral which generally occurs in three types: antigorite, chrysotile, and lizardite. It commonly contains 32–38% MgO and 35–40% SiO2 with minor amounts of Fe, Al, Ca, Cr, and Ni.1–4 Currently, serpentine has mainly been used as: the flux in blast furnaces in the iron and steel industry, a road construction material, foundry sand, fertilizer, and for soil amendment etc.5,6

Several studies have been carried out to extend the utilization of serpentine mineral. Pundac has developed a method for recovering silica, iron oxide and magnesium carbonate from serpentine using ammonium bisulfate.7 Noranda has proposed the Magnola process to produce magnesium metal from chrysotile serpentine and asbestos tailing.8 The Magnola magnesium plant with a capacity of 58,000 t/yr was started up in 2000, but was closed in 2003 after operating for about two years. Kosuge et al. have extensively studied the preparation of magnesium sulfate, amorphous silica and siliceous porous materials by acid treatment of the serpentine mineral.9 Kim et al. have conducted research on the synthesis of zeolite using highly porous amorphous silica obtained from serpentine by hydrochloric acid treatment.10

As interest increases in the capture and storage of CO2, one of greenhouse gases linked to global warming, the availability of serpentine mineral for sequestering CO2 emissions generated from fossil fuel combustion has been investigated.11–14 Sequestration of CO2 using serpentine mineral provides safe, long-term storage for CO2 as CO2 is immobilized into the mineral by the carbonation reaction to form thermodynamically stable MgCO3. Among the carbonation routes for serpentine that have been studied, the most promising one seems to be the aqueous mineral carbonation process, which includes the extracting of Mg from serpentine minerals and the subsequent carbonation reaction with CO2 to form the geologically stable mineral MgCO3.

The rate-determining step in the aqueous carbonation of serpentine minerals is the dissolution of Mg from serpentine.11 Thus, the fundamental characteristics of the dissolution of Mg from serpentine, which is very important to the optimization of the mineral CO2 sequestration using serpentine, should be well understood. There have been several studies on the dissolution mechanisms and kinetics of Mg from serpentine in acid solutions, but most of them involved the pre-treatment of the mineral, which affected the dissolution of the Mg.15–17 Teir et al. have recently reported that the dissolution kinetics of Mg from natural serpentine in acids follows a shrinking unreacted-core model with product layer diffusion as the rate-determining step.18 In that study, the serpentine particles were assumed to be spherical in shape,18 but serpentine is known to have a layered crystal structures formed by the alternate stacking of the tetrahedral silica and octahedral brucite layers.1,19 Therefore, taking the crystal structure of serpentine into account, further studies are required to completely elucidate the dissolution of Mg from serpentine in acids.

The present study aimed to examine the behavior of Mg during H2SO4 dissolution of the serpentine mineral distributed in Korea. The effects of H2SO4 concentration, dissolution temperature, and agitation speed on the dissolution of Mg were investigated. The dissolution kinetics of Mg reported in this paper was determined by minimizing the effects of the film boundary diffusion and particle size. In addition, the mechanochemo-mechanical effect on the dissolution of Mg was investigated. The study is expected to provide useful data for the optimization of H2SO4 dissolution of Mg to effectively utilize Korean serpentine mineral in CO2 sequestration through the aqueous carbonation process.

2. Experimental

2.1 Materials

The serpentine ore distributed in the Andong area, Korea, was selected for this study. It was ground by a ball mill, and then sieved to smaller than 45 μm (average particle size 20.6 μm). The X-ray pattern (see Fig. 1) of the serpentine
ore shows that it is composed mainly of antigorite with minor lizardite, magnetite (Fe3O4), tremolite [Ca2Mg5Si8O22(OH)2], and diopside (MgCaSi2O6). The chemical composition of the serpentine sample which was used is shown in Table 1. It contained 19.96 mass% Mg, 17.52 mass% Si, 7.99 mass% Fe, and 2.81 mass% Al. The weight loss of serpentine on ignition for 1 h at 900 °C under a nitrogen atmosphere was 8.90 mass%.

### 2.2 Procedures

Experiments on the dissolution of serpentine in H2SO4 solution were carried out in a 1 L three necked Pyrex reactor immersed in a thermostatic water bath. The reactor was fitted with an agitator and reflux condenser. The reflux condenser was inserted in one port to avoid solution losses at high temperatures. In a typical run, 500 mL of acid solution (0.10–3.00 M H2SO4) was poured into the reactor and allowed to reach thermal equilibrium (25–90°C). 2.00 g of serpentine was then added to the reactor, and the agitator was set to 400 rpm. During the experiment 4 mL of the solution sample was taken periodically at a desired time interval (5–120 min) with a syringe. The sample was filtered and then 3 mL of the filtrate was diluted with 5% HCl solution for the chemical analysis.

The milling of serpentine was conducted using a planetary ball mill (Pulverisette 5, Fritsch GmbH) to investigate the mechanochemical effect on the dissolution of Mg in H2SO4 solution. 25 g of the serpentine sample was placed to a jar (250 mL inner volume) with 13 zirconia balls (20 mm diameter). The milling was carried out batch-wise for different periods of time (30–120 min). The rotation speed of the mill was kept at approximately 150 rpm. Dissolution experiments with the mechanically activated serpentine were carried out using a 0.5 M H2SO4 solution by the procedure described above.

The sample solutions were analyzed by an atomic absorption spectrometry (AA, SpectrAA400, Varian Inc.) and an inductively coupled plasma-atomic emission spectrometry (ICP-AES, JY-38 plus, Jobin Yvon Ltd.). The serpentine sample was also characterized by X-Ray Diffractometry (XRD) (D-max-2500PC, Rigaku Co.).

### 3. Results and Discussion

Serpentine is a sheet silicate mineral with a 1:1 structure by the alternate stacking of the tetrahedral silica and octahedral brucite [Mg(OH)2] layers linked into sheets. Under acidic conditions, brucite layers of Mg(OH)2 dissolves from serpentine, leaving the silica as a product layer.8,19) The dissolution reaction of Mg from serpentine in H2SO4 solution can be expressed as follows:

\[
\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 3\text{H}_2\text{SO}_4 \rightarrow 3\text{Mg}^{2+} + 3\text{SO}_4^{2-} + 2\text{SiO}_2 + 5\text{H}_2\text{O}
\]  

(1)

#### 3.1 Dissolution of natural serpentine ore

The dissolution of Mg at agitation speeds in the range 200–600 rpm was tested to investigate the effect of liquid film boundary diffusion surrounding solid particles on the rate of dissolution of Mg from natural serpentine particles in 0.5 M H2SO4 at 50°C. As can be seen from Fig. 2, the results indicate that the dissolution rate is independent of the agitation speed at speeds higher than 300 rpm. Therefore, in all subsequent dissolution experiments, a working agitation speed of 400 rpm was selected to ensure effective particle suspension in the solution while minimizing the effect of liquid film boundary diffusion surrounding the solid particles.

The dissolution of Mg from natural serpentine ore was investigated at H2SO4 concentrations of 0.1–3.0 M at 50°C. Figure 3 shows the effect of H2SO4 concentration on the dissolution of Mg. The fraction of Mg dissolved increased as the concentration of H2SO4 increased. As shown in Fig. 3, the rate of dissolution of Mg was initially (in the first 20–
30 mins) found to be a little fast, but then slowed down slightly as the dissolution time increased. The fraction of Mg dissolved increased from about 45% to about 85% as the \( \text{H}_2\text{SO}_4 \) concentration increased from 0.1 M to 3.0 M for a dissolution time of 120 min.

Figure 4 shows the effect of temperature on the dissolution of Mg from the natural serpentine ore in 0.5 M \( \text{H}_2\text{SO}_4 \). The dissolution temperature varied in the range 25–90 °C, while all other parameters were kept constant. It can be seen from Fig. 4 that higher temperatures yielded higher dissolution rates of Mg from the serpentine. At 50 °C the fraction of Mg dissolved was about 60% in 120 min, while complete dissolution of Mg was achieved in 30 min when the dissolution temperature was increased to 90 °C.

### 3.2 Dissolution of milled serpentine ore

In order to enhance the rate of dissolution of Mg from natural serpentine ore in \( \text{H}_2\text{SO}_4 \) solution, it was mechanically activated by a planetary ball mill. Figure 5 shows the dissolution behavior of Mg from the milled serpentine ore in 0.5 M \( \text{H}_2\text{SO}_4 \) solution at 50 °C as a function of the milling time. The milling time for the mechanical activation of natural serpentine ore was varied up to 120 min. As shown in Fig. 5, appreciable enhancement of Mg dissolution was achieved through the mechanical activation of natural serpentine ore by the milling. The speed of the dissolution of Mg in 0.5 M \( \text{H}_2\text{SO}_4 \) solution increased initially (for the first 20 min) as the milling time for the natural serpentine ore increased. Based on the interpretation by Zhang et al., the somewhat faster dissolution rate of the milled serpentine ore may explain why the structure of natural serpentine ore was transformed from a crystalline state into an amorphous one through the mechanical activation, which was not clearly verified in this work. Zhang et al. have reported that the considerable enhancement of the dissolution of Mg from milled serpentine arises from the structural transformation of natural serpentine by milling, and that structural transformation is caused by the disordering around the Mg local structure caused by the release of the OH base from the Mg octahedron.

Figure 6 shows the effect of dissolution temperature on the dissolution of Mg from the milled serpentine ore in 0.5 M \( \text{H}_2\text{SO}_4 \) (Milling time = 30 min).
H$_2$SO$_4$. The serpentine ore was mechanically activated by the milling at a rotational speed of 150 rpm for 30 min. Figure 6 shows that the dissolution rate of Mg from the milled serpentine ore increased remarkably as the dissolution temperature increased. Based on the results shown in Figs. 4 and 6, it was found that the fraction of Mg dissolved from the milled serpentine ore was a little higher than that from the natural serpentine ore in 0.5 M H$_2$SO$_4$ at a dissolution temperature of 25–70°C. However, it was observed that there was little mechanochemical effect on the dissolution of Mg in H$_2$SO$_4$ solution when the dissolution temperature was increased to 90°C. This suggests that more information is required about the feasibility of using mechanical activation to enhance the rate of dissolution of Mg from serpentine.

### 3.3 Kinetic analysis

The interpretation of the dissolution kinetics of Mg has been based on the experimental data for the dissolution of Mg from serpentine and its textural structure. The textural structure of serpentine mineral with a 1:1 structure due to the alternate stacking of the tetrahedral silica and octahedral brucite is shown in Fig. 7. In the H$_2$SO$_4$ dissolution of serpentine ore, Mg in the brucite layer between the silica layers dissolves in the acid solution, while the silica which has not dissolved in the acid solution forms thin channels by maintaining its own morphology. Thus, it was assumed that the dissolution of Mg from serpentine ore in the acid solution proceeds by the diffusion of the acid solution throughout the thin channels formed between the silica layers which may act as a diffusion barrier of H$_2$O$^+$ ions. Based on that observation, the Jander rate equation is expected to best represent the dissolution reaction of Mg from serpentine ore in H$_2$SO$_4$ solution. This was verified after trying a number of different rate expressions such as: the spherical shrinking unreacted-core expression, and the nucleation and growth equation. The Jander rate equation was derived from the reactions controlled by a fluid diffusion mechanism. This rate expression can be expected to be applicable because the volume change of serpentine particles before and after the dissolution of Mg in H$_2$SO$_4$ solution is negligible, as can be seen indirectly from the texture of the serpentine ore in Fig. 7. In this rate expression for a spherical particle of serpentine ore, the fraction of Mg dissolved from the serpentine is related to the dissolution time by the expression:

$$[1 - \left(1 - X_{Mg}\right)^{1/3}]^2 = k_{app}t$$  \hspace{1cm} (2)

In this equation, $X_{Mg}$ is the fraction of Mg dissolved, $t$ is the dissolution time (min), and $k_{app}$ is the apparent rate constant (min$^{-1}$) which is given by

$$k_{app} = bk f(C_{H_2SO_4}) = bk C_{H_2SO_4}^n$$  \hspace{1cm} (3)

Where $b$ is the stoichiometry factor ($b = 1/3$ in the serpentine–H$_2$SO$_4$ system, according to the formulation by Sohn$^{22}$) for eq. (1), $k$ is the intrinsic rate constant (min$^{-1}$·mol$^{-n}$), $C_{H_2SO_4}$ is the concentration of H$_2$SO$_4$, $f$ is the dependence of the concentration of the rate, and $n$ is the reaction order for the H$_2$SO$_4$ concentration. It is apparent from eq. (2) that a plot of $[1 - \left(1 - X_{Mg}\right)^{1/3}]^2$ vs. $t$ should be linear with $k_{app}$ as the slope. The validity of the Jander rate expression for the dissolution of Mg from the serpentine in H$_2$SO$_4$ solution was verified by plotting curves of the dissolved Mg versus time of Figs. 3, 4 and 6 according to eq. (2), as shown in Figs. 8–10. In the present study, the fraction of Mg dissolved up to 0.90 was investigated for the kinetic analysis of the dissolution reaction. Figures 8–10 indicate that the rate of dissolution of Mg is limited by the thin channels formed between silica layers that are not dissolved by H$_2$SO$_4$ solution, as explained previously.

In order to evaluate the dependence of the H$_2$SO$_4$ concentration of $k_{app}$, the values of $k_{app}$ obtained in Fig. 8 was plotted in Fig. 11 as $lnk_{app}$ against $lnC_{H_2SO_4}$. As shown...
In Fig. 11, the reaction order $n$ in eq. (3) is obtained to be 0.57 from the slope. Thus, eq. (3) can be rewritten as:

$$k_{\text{app}} = \frac{1}{3} k C_{\text{H}_2\text{SO}_4}^{0.57} \text{ (min}^{-1})$$

(4)

The values of $k$ at different temperatures were calculated using eq. (4) from the slopes of each straight line in Figs. 9 and 10. Figure 12 shows the Arrhenius plots of the rate constants. The slopes of the straight line placed through the experimental points yield activation energies of 82.0 kJ/mol for the natural serpentine–H$_2$SO$_4$ system and 76.7 kJ/mol for the milled serpentine–H$_2$SO$_4$ system, respectively.

As shown in Fig. 12, the activation energy obtained from the Mg dissolution experiments of the milled serpentine ore is a little low compared with that obtained from the experiments with the natural serpentine ore. Thus, it was considered that the fraction of Mg dissolved from the milled serpentine is a little higher than that from the natural serpentine, as explained previously. The rate constants $k$ for the natural serpentine–H$_2$SO$_4$ system and the milled serpentine–H$_2$SO$_4$ system at different temperatures calculated on the basis of eq. (4) can be expressed by the following equation:

For the natural serpentine–H$_2$SO$_4$ system

$$k = 7.2 \times 10^{10} \cdot \exp\left(\frac{-9,862.4}{T}\right) \text{ (min}^{-1}\text{.mol}^{-0.57})$$

(5)

For the milled serpentine–H$_2$SO$_4$ system

$$k = 1.5 \times 10^{10} \cdot \exp\left(\frac{-9,225.0}{T}\right) \text{ (min}^{-1}\text{.mol}^{-0.57})$$

(6)

Where all the activation energy obtained is a little higher than measured in many cases of diffusion-controlled leaching. In this research, the reason for that was not clearly determined.$^{19,23}$ It may be due to some forms of surface diffusion of Mg$^{2+}$, H$_3$O$^+$, and SO$_4^{2-}$ ions in the thin channels formed between the silica layers during the dissolution of Mg, which has a high activation energy. On the other hand, a number of researchers have also reported a high activation energy for the diffusion-controlled leaching. Teir et al. have reported that the activation energies for the diffusion-controlled leaching of Mg from natural serpentinite in several acid solutions are 68–74 kJ/mol.$^{18}$ Hernández et al. have also reported that the leaching of Mg from sepiolite with H$_2$SO$_4$ has an activation energy of 63.5 kJ/mol,$^{19}$ which is controlled by diffusion of the acid.
solution. It has also been reported that the activation energies for the diffusion-controlled leaching of iron oxides with HCl are 62–79 kJ/mol.\(^{23}\)

Using eqs. (2) and (4)–(6), the fraction of Mg dissolved from serpentine ore in \(\text{H}_2\text{SO}_4\) solution is, respectively, represented by the following equation:

For the natural serpentine–\(\text{H}_2\text{SO}_4\) system

\[(1 - (1 - X_{\text{Mg}})^{1/3})^2 = k_{\text{app}}t\]  \((7)\)

Where

\[k = 2.4 \times 10^{10} \cdot \exp\left(\frac{-9,862.4}{T}\right) \times C_{\text{H}_2\text{SO}_4}^{0.57} \text{ (min}^{-1})\]

For the milled serpentine–\(\text{H}_2\text{SO}_4\) system

\[(1 - (1 - X_{\text{Mg}})^{1/3})^2 = k_{\text{app}}t\]  \((8)\)

Where

\[k = 5.0 \times 10^9 \cdot \exp\left(\frac{-9,225.0}{T}\right) \times C_{\text{H}_2\text{SO}_4}^{0.57} \text{ (min}^{-1})\]

4. Conclusions

The behavior of Mg during \(\text{H}_2\text{SO}_4\) dissolution of the serpentine mineral which occurs in Korea was investigated under differing conditions in a stirred batch reactor. In 0.5 M \(\text{H}_2\text{SO}_4\), complete dissolution of Mg from the natural serpentine was achieved after 30 min at a dissolution temperature of 90°C. The fraction of Mg dissolved from the milled serpentine was a little higher than that from the natural serpentine in 0.5 M \(\text{H}_2\text{SO}_4\) at dissolution temperatures up to 70°C, whereas the increase in the fraction of Mg dissolved was negligible at 90°C. The dissolution kinetics of Mg were found to follow the Jander equation with the diffusion of \(\text{Mg}^{2+}\), \(\text{H}_3\text{O}^+\), and \(\text{SO}_4^{2-}\) ions throughout the thin channels formed between the silica layers in the serpentine particles acting as the rate-controlling step. The activation energies of the dissolution were calculated to be 82.0 kJ/mol for the natural serpentine–\(\text{H}_2\text{SO}_4\) system and 76.7 kJ/mol for the milled serpentine–\(\text{H}_2\text{SO}_4\) system, respectively. The reaction order with respect to \(\text{H}_2\text{SO}_4\) concentration in the solution was found to be 0.57.

Acknowledgements

This research was supported by the Basic Research Project of the Korea Institute of Geosciences and Mineral Resources (KIGAM) funded by the Ministry of Knowledge and Economy of Korea. The authors would like to thank Dr. Young-nam Jang and Dr. Sujeong Lee for providing valuable comments.

REFERENCES